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Investigation of photo-induced absorption in a $Bi_{12}TiO_{20}$ crystal

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ABSTRACT A photorefractive $Bi_{12}TiO_{20}$ (BTO) crystal is exposed with high intensity pulsed-laser beams 532 nm (the average intensity of the laser was 110 mW/cm^2, the average intensity per pulse was 2 MW/cm^2), and the photo-induced dynamics of the absorption between 480 and 900 nm are studied and explained by two long-lived energy levels in the forbidden band. The relaxation times of the long-lived energy levels are experimentally found to be 10^4 and 10^5 s. The hysteresis character of the absorption coefficient is discussed.

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1 Introduction

The photo-induced absorption is the change of the absorption of light as the result of irradiation. Any influence of the light on the internal structure of the photorefractive crystals, which is connected with the energy redistribution of charge carriers can change the absorption. The temporal and amplitude behavior of this effect depends strongly on the energy levels and the relaxation characteristics of the materials. Most of the characteristic effects are often disregarded in the quasi-stationary processes because of their short lifetime in the range of 1–100 ps or weak exposure intensities [1]. Sometimes the induced absorption can have lifetimes between seconds and even days.

In 1988 Brost et al. [2, 3] studied the intensity dependent absorption in $BaTiO_3$ and attributed it to the presence of secondary photorefractive centers. These are intermediate-level traps that are highly ionized at room temperature and therefore can compete for free carriers generated by photoexcitation of the deep traps [3]. In 1990 the same group measured the spectral and temporal characteristics of the photo-induced absorption in $BaTiO_3$ [4]. Increasing of absorption was observed in the Vis and the near IR. The lifetime of the induced absorption was about several seconds. They suggested that iron or iron-oxygen vacancy defects were responsible for the absorption as Faughnan described it for $SrTiO_3$ in 1971 [5]. An analogous charge transport model was used later in 1991 by Holtmann et al. [6] to explain the light-induced absorption in $KNbO_3$:Fe crystals. In 1994 Simon et al. [7] experimentally investigated the light-induced absorption in $LiNbO_3$:Fe and $LiNbO_3$:Fe:Me crystals generated by a pulse laser. For the theoretical description a two-center charge transport model as for $BaTiO_3$ [2, 3] and $KNbO_3$ [6] was developed and applied. Orlov et al. experimentally found a similar increase of absorption in $Sr_{0.59}Ba_{0.41}Nb_2O_6/Sr_{0.75}Ba_{0.25}Nb_2O_6$ and $Pb_{0.5}Ba_{0.5}Nb_2O_6$ in 1994 [8] and by Liu et al. in 1998 [9], respectively. In 1999 Kobozev et al. investigated light-induced absorption in $Bi_{12}TiO_{20}$ (BTO) [10] and tried to describe the effect by three-valence-states impurity-centers in combination with shallow traps. In 2000 Wevering et al. [11] investigated the light-induced absorption generated by a pulse UV Nd:YAG laser in $LiTaO_3$. For the theoretical description the same model as for $LiNbO_3$ crystals was proposed. The lifetimes of the induced absorptions in $LiTaO_3$ and $LiTaO_3$ were about 10–100 µs. In 2003 Marinova et al. studied light-induced properties of $Bi_{12}TiO_{20}$:Ru and showed the influence of impurity concentrations on absorption and photo-induced absorption [12]. In 2002 Shandarov et al. [13] investigated experimentally the photo-induced absorption in $Bi_{12}TiO_{20}$:Ca and suggested a three-level model, which is a special case of the two-center model. The lifetime of the induced absorption was about several hours and depended on the temperature [14]. In 2005 they reported the photo-induced absorption in planar waveguides based on $Bi_{12}TiO_{20}/Bi_{12}SiO_{20}$ and $Bi_{12}TiO_{20}$:Cu/$Bi_{12}SiO_{20}$ crystals [15]. In 2007 we investigated the spectral characteristics of the photo-induced absorption in the pure $Bi_{12}TiO_{20}$ using pulse lasers and calculated the energy of the absorption centers [16]. It should be noticed that photo-induced absorption in $Bi_{12}TiO_{20}$ crystals was experimentally already in the past and was described as the reason for the absorption grating [17, 18].

Photorefractive crystals are promising candidates for various applications as media for dynamic holography, optical information processing, phase conjugation, holographic interferometry and others. One of the most important questions for their application is the corresponding response time. Crystals of the sillenite group like $Bi_{12}SiO_{20}$ (BSO) and $Bi_{12}TiO_{20}$ (BTO) can reach low response times if pulse laser systems are applied. Unfortunately, the high peak intensity of pulse laser

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radiation generates strong photo-induced absorption, which influences negatively on the whole system. In this case the spectral and dynamical behaviors of the induced absorption are of great importance.

In 2005 we investigated the response rate of the photorefractive nonlinearity in BTO with pulse lasers (532 nm, length of pulses 20–80 ns) [19] and could demonstrate the great influence of the induced absorption on the multiwave mixing optical system. The corresponding spectral characteristics of the induced absorption generated by a pulse laser were presented in [16].

In this paper we investigate the dynamical characteristics of the photo-induced absorption produced by pulse lasers in a BTO crystal with a lifetime of the induced effect in the order of hours. We characterize experimentally the internal system of the energy levels and find experimentally to our knowledge for the first time the dynamic characteristics of each type of long-lived traps, based on a two-center model in a wide spectral region. The hysteresis character of the photo-induced absorption is also shown.

2 Photo-induced absorption in a BTO crystal generated by pulse lasers

The investigation of the photo-induced absorption in BTO was carried out for a nominally pure $Bi_{12}TiO_{20}$ crystal, which was grown from a congruent melt by the Czochralski method. The crystal has the cubic symmetry 23 like the other members of the sillenite family. The light radiation propagated along the [100] crystallographic axis. The (100) faces with the transverse dimensions $7 \times 7\ mm^2$ were polished with optical quality. The thickness of the crystal with regard to the dimension [100] was 2.8 mm. For inducing of the absorption a pulse laser at 532 nm (second harmonic of Nd:YAG) (Fig. 1a) was applied. An aperture of 2.5 mm cuts out the spatially homogeneous part of the laser beam. The pulse duration was 30–50 ns, the repetition rate was 10 Hz, and the average pulse energy after passing through the diaphragm was 0.5 mJ. The average power of the pulse was 0.13 MW. So, the average intensity of the laser radiation incident on the surface of the crystal during the pulse was $2\ MW/cm^2$. The integral average intensity of the laser radiation incident on the crystal during exposition was $110\ mW/cm^2$. The polarization of the laser light was located in the plane (100) and parallel to [011].

The absorption of the crystal was measured with a spectrophotometer based on a CCD line array with 2048 pixels. The dispersion element was a fixed diffraction grating with 600 lines/mm yielding a resolution < 1 nm. The probe beam consisted of light emitted by a Xe and halogen lamp (Xe/HL) simultaneously with a total intensity below $0.8\ mW/cm^2$ in the whole spectral range. Five seconds after the irradiation with the laser (532 nm) the spectrophotometer and the Xe/HL were switched on, and the absorption was measured in the range 480–1100 nm. The integration time of the CCD array was 11 ms, which gives a time of measurement of 0.11 s for 10 single measurements. After each cycle of measurement the laser was turned on for 5 s and the irradiation continued. The relaxation of the induced absorption was found to be constant in the darkness and at fixed room temperature. Within the Vis a long-lived photo-induced absorption appears which could be measured using the setup shown in Fig. 1b. In this case the laser beam was focused by a micro objective into a spot of 0.2 mm diameter.

2.1 *Excitation*

The spectra of the photo-induced absorption against the exposition energy are shown in Fig. 2. A change of absorption became detectable already after 1 min of exposition (total energy per square centimeter – ca. 7 J).

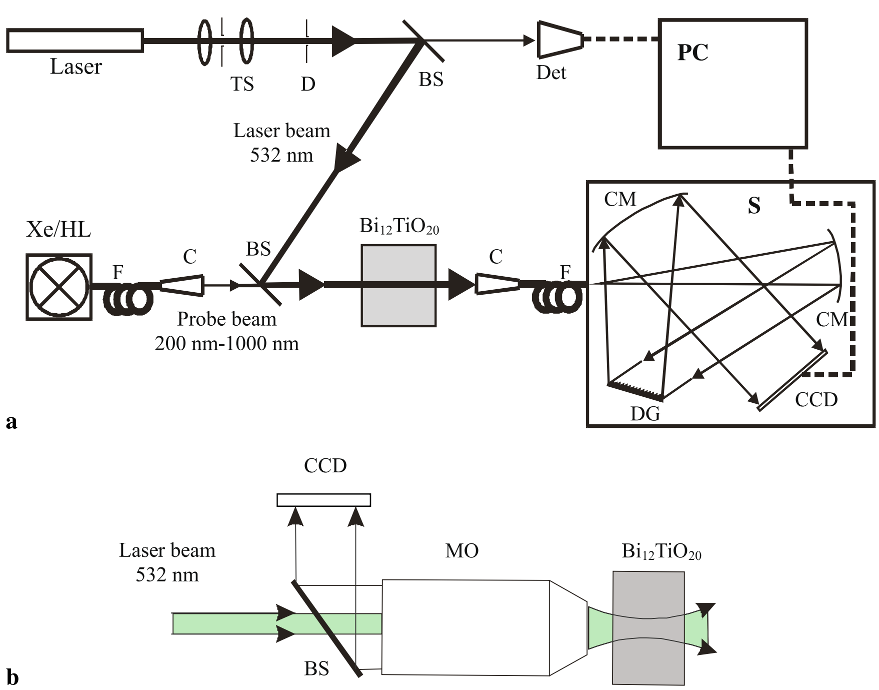


FIGURE 1 (**a**) Scheme of the experimental setup for the generation and measuring of the photo-induced absorption. Laser – Nd:YAG (532 nm); TS – telescopic system; D – diaphragm; BS – beam splitter; Xe/HL – Xe/halogen lamp (200–1000 nm); F – fiber optics; C – collimator; S – spectrophotometer; CM – collimating mirror; DG – diffraction grating; CCD – CCD linear array "Sony 2048"; Det – photo detector; PC – computer. (**b**) Scheme of the experimental setup for visualization of the photo-induced absorption in the Vis. MO – micro objective; CCD – CCD matrix 1400×1400 pixel

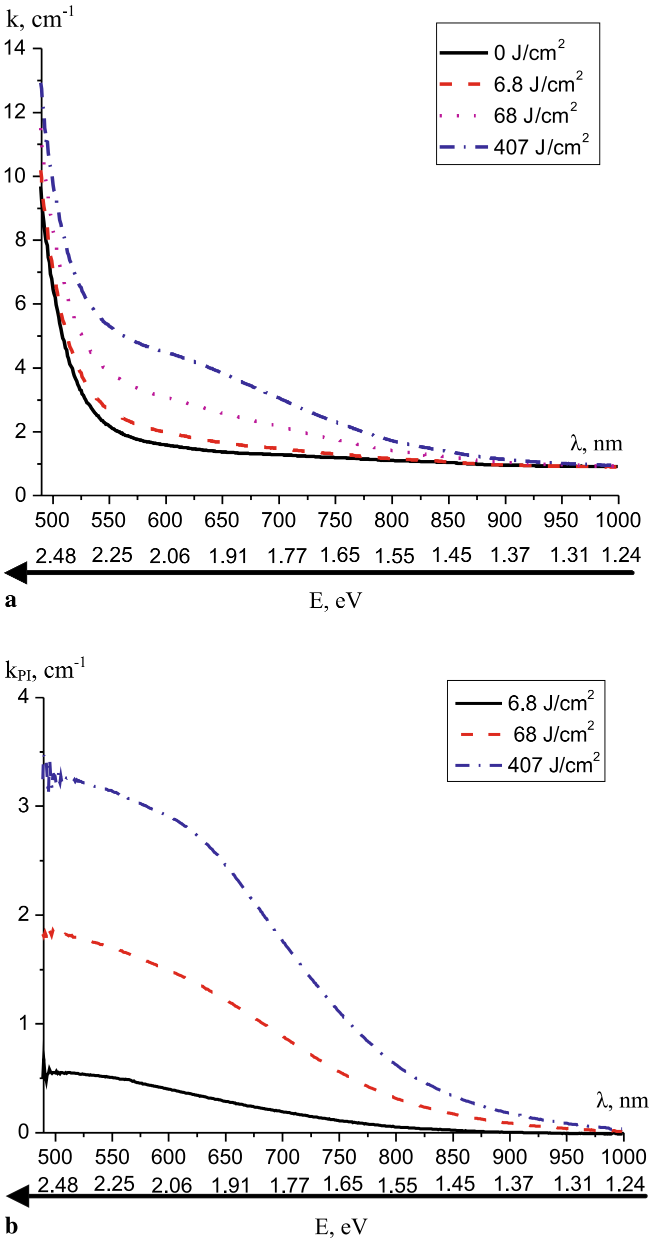


FIGURE 2 (**a**) Absorption spectrum of BTO for different values of the total exposition (J/cm^2). k is the absorption coefficient. (**b**) Dependence of the photo-induced absorption k_{PI} (difference between integral absorption k and initial absorption without exposition k_0). The pulse laser had an average intensity of 110 mW/cm^2 at 532 nm

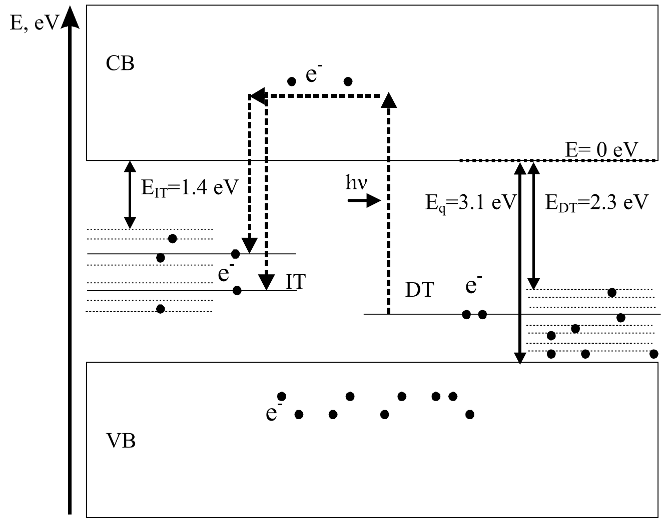


FIGURE 3 Schematic illustration of the photo-induced absorption in BTO. The long-lived intermediate traps (IT) are located in the forbidden band and are responsible for the stronger increasing of the photo-induced absorption in the Vis and near IR spectral ranges. E_q – width of the forbidden band; E_{DT} – depth of the upper border of the deep levels; E_{IT} - depth of the upper border of the levels of the long-lived centers (intermediate-level traps)

One can observe a strong increasing of the absorption in the range up to 900 nm during the light exposition. This effect can be explained by long-lived centers with energy levels in the forbidden band that are caused by impurities and defects in the bulk of the crystal [20]. These centers can be denoted as intermediate-level traps (IT) [2, 3] (Fig. 3).

Under normal conditions at room temperature and without pre-exposure the absorption is coursed only by the excitation of charges from deep levels (deep traps DT) and from the valence band (VB) to the conducting band (CB) [21]. The DT can be attributed to the spreading of the VB due to impurities and defects. The population of the DT is due e.g. to a stochastic excitation of charges from the VB and is much weaker than the population of the VB. The spectrum of the non-photo-induced absorption (Fig. 2a) shows that the upper level of the DT lays at ca. 2.3 eV (ca. 540 nm) below the CB. The width of the forbidden band of BTO crystals is approximately 3.1 eV (ca. 400 nm) [22]. It was shown by Oberschmid [23] for bismuth oxides of the type $Bi_{12}MO_{20}$ (where M = Ge, Si or Ti) that the incorrect occupation by Bi_M is responsible for the light absorption in the region between 2.3 eV and 3.2 eV and causes the DT.

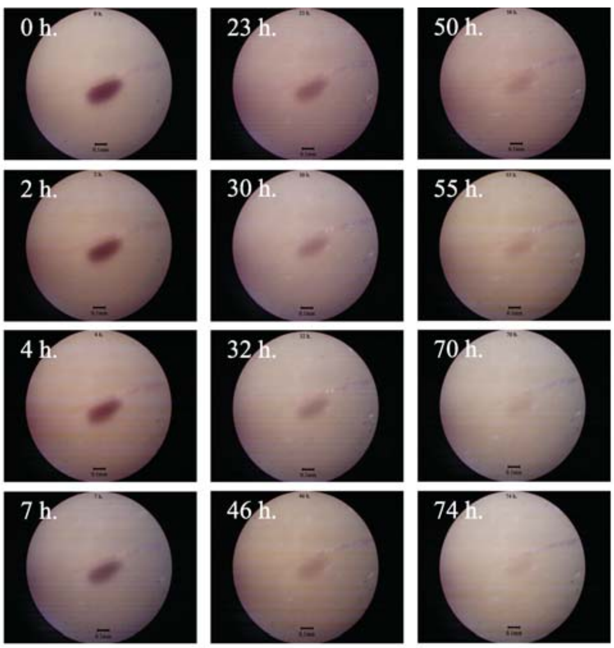
The undoped BTO is an n-type photoconductive crystal under illumination with green light [24]. In our case for an irradiation at 532 nm the excitation of electrons basically takes place from the DT to the CB. If the charges are excited into the CB they can recombine back to the VB and DT as well as to the long-lived IT. The lifetime of charges in the CB is relatively short because of the short recombination time constant τ_r, which is below 100 ns [19, 25]. The charges of the long-lived levels can be excited again into the CB by photons with lower energy. A growth of the photo-induced absorption k_{PI} is observed at wavelength below 900 nm (Fig. 2b). The photo-induced absorption k_{PI} is connected with the excitation of charges from the IT to the CB. It will be shown below that there are two different long-lived levels in the system of IT. The upper level border of the long-lived levels lays at ca. 1.4 eV (900 nm) below the CB (Fig. 2b). We must not take into account the excitation of electrons from VB to CB and to IT because the excitation wavelength is too less for the corresponding excitation of electrons. So, the transition of electrons is neglected in our case. If we would have a significant excitation of electrons from VB to IT a strong absorption would appear in a non-excited crystal and could be observed in the corresponding spectrum. A schematic illustration of the photo-induced absorption is shown in Fig. 3. Investigations of Reyher et al. and Vogt et al. [26, 27] show that the nature of the IT is determined by a Bi^{3+} ion associated with a hole, whereas the hole is mainly localized at the oxygen neighbors.

2.2 *Relaxation*

The BTO crystal shows slow relaxation characteristics and keeps the absorption induced during the exposition by laser pulses with a relatively high intensity (2 MW/cm^2) for a long time (till 80 h). E.g. the induced absorption in Vis and its dynamics of relaxation can be seen in Fig. 4a. The dependence of the spectrum of the induced absorption in BTO versus the relaxation time is shown in Fig. 4b.

The absorption coefficient k for a wavelength in the case of the transition between two fixed energy levels is given by

$$k = (n_1 - n_2)\sigma \approx n_1\sigma , \qquad (1)$$



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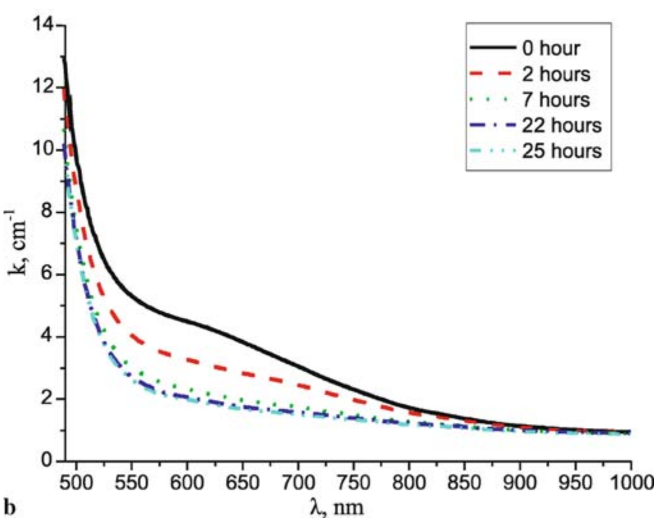


b

FIGURE 4 (**a**) View of the crystal with photo-induced absorption in its center. A microscope took the images during the relaxation process. The laser radiation was focused to a spot size of 0.2 mm. (**b**) Absorption spectrum for different relaxation times after laser exposition during 1 h with an average intensity of 110 mW/cm^2 at the wavelength 532 nm (exposition was approx. 400 J/cm^2). k is the coefficient of absorption

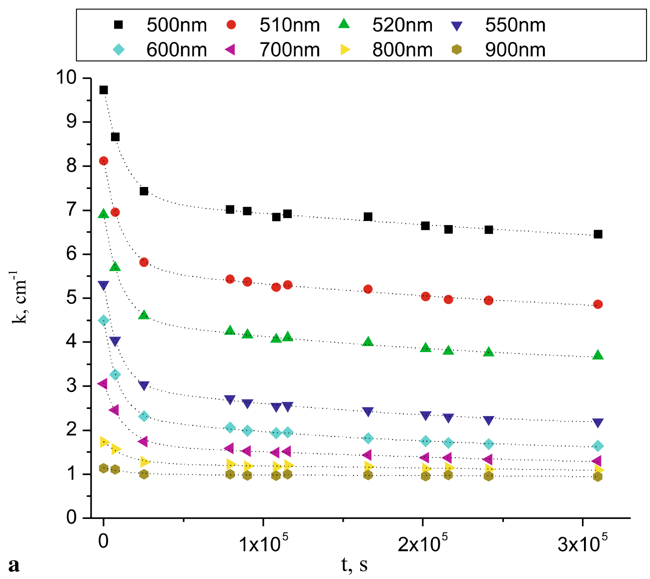
where n_1 is the population of the lower level (quantity of the absorption centers), n_2 is the population of the upper level (quantity of the emitting centers), and σ is the cross-section of absorption. The right side of the equitation (1) is true when the population of the lower level is much higher than the upper ($n_2 \ll n_1$) as in our case.

The population of the long-lived levels decreases as a result of thermal processes in darkness and can be described by

$$n = n_0 e^{-t/\tau} , \qquad (2)$$

where n_0 is the population of the level at the beginning, t is the time, and τ is the lifetime of charge carriers on the trap level. Figure 5a shows the temporal development of the coefficient of absorption for different wavelengths during relaxation.

Analyzing the relaxation dynamics presented in Fig. 5a, we can show that it can be approximated by a double-



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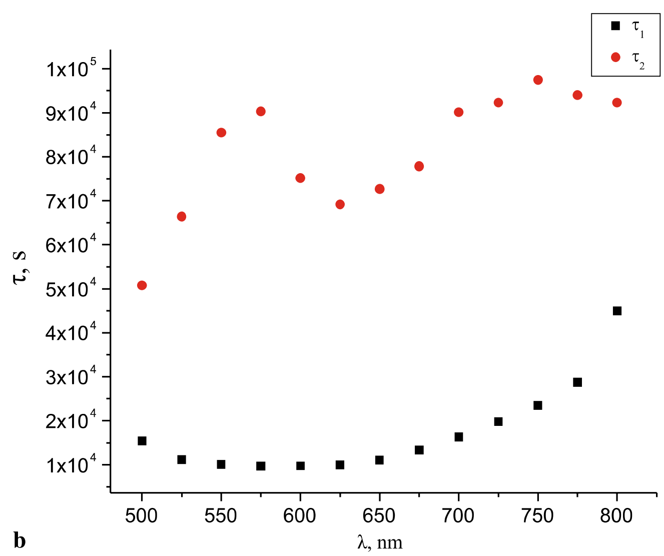

b

FIGURE 5 (**a**) Dependence of absorption on the relaxation time for different wavelengths after laser exposition during 1 h with an average intensity of 110 mW/cm^2 and a wavelength 532 nm. (**b**) Spectral dependence of the lifetimes τ_1 and τ_2 of the long-lived levels exponential function (dotted line):

$$k = k_0 + k_1 e^{-t/\tau_1} + k_2 e^{-t/\tau_2} , \quad (3)$$

where $k_0, k_1, k_2, \tau_1, \tau_2$ are the mathematical coefficients of approximation. It is possible to find a relationship between the coefficients of approximation and the physical magnitudes: k_0 is the coefficient of absorption without the photo-induced effect, k_1, k_2 are the initial coefficients of absorption for long-lived levels, τ_1, τ_2 are the corresponding times of life. There are two relaxation components ($k_1 e^{-t/\tau_1} + k_2 e^{-t/\tau_2}$). Each of them is connected with a specific type of absorption centers. Using the experimental values (Fig. 5a) and (3) the spectral dependences of lifetimes of the long-lived levels can be found (Fig. 5b).

The two "spectra" of lifetimes for the two kinds of induced long-lived centers can be seen in Fig. 5b. In our case the dependences of the lifetimes on the wavelengths are nonlinear and non-monotone, which is in agreement with the stochastic nature of the traps. A random variation of the surrounding of each center yields to a broadening of the levels of the traps. Moreover, the variation of the surrounding influences on the lifetimes of centers and gives dispersion of the energy level of each center. Figure 5b shows that the lifetime of the trap depends on its location depth in the forbidden band. This is explicitly expressed for the second type of traps with longer lifetimes.

2.3 *Hysteresis*

It is found that the lifetimes differ by one order for both components and depend on the wavelength. This could be connected with the difficult structure and the high vacancy of the tetrahedral lattice of sillenites [20]. The multi-centered nature of photo-induced absorption was additionally proved by comparison of the absorption for different wavelengths. The phase-plane picture of the system for basic parameters: (absorption at 600 and 800 nm) is shown in Fig. 6. At the wavelengths 600 and 800 nm, the effect of hysteresis can be clearly seen. The existence of two different ways of evolution during inducing and relaxation of absorption (hysteresis) is the consequence of the multilevel structure of the long-lived levels in the forbidden band of the crystal. During relaxation the redistribution of charge carriers takes place between different levels with various spectral and temporal properties.

Thus, from the observations of the dynamics of the photo-induced absorption one can conclude about the multicentered nature of the long-lived levels in the forbidden band of BTO. At the same time the intraband transportation of energy results in a hysteresis behavior of the dark relaxation of the induced absorption relative to the stimulation of the effect.

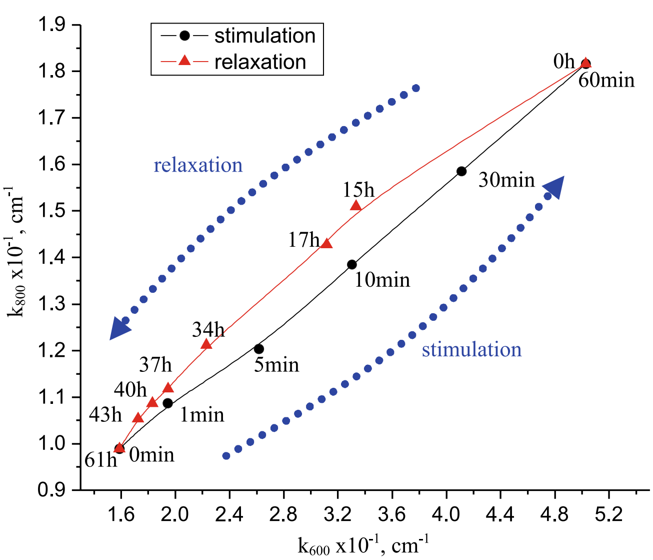

FIGURE 6 Dependence of the absorption coefficient for the wavelength 800 nm on the absorption coefficient for the wavelength 600 nm (bistability). The stimulation was realized with a pulse laser (average intensity – 110 mW/cm^2, 532 nm) during 1 h. The relaxation was studied during 61 h

3 Conclusion

In conclusion, we exposed a BTO crystal with high intensity pulsed-laser beams (110 mW/cm^2 at 532 nm) and investigated the photo-induced absorption. We noticed that the absorption increased stronger up to 900 nm and explained this effect by the existence of long-lived levels in the forbidden band, where the charges are collected after quick relaxation from the conducting band. Analyzing the relaxation times for different wavelengths, we experimentally found that there are primarily two long-lived centers (levels) with lifetimes of ca. 10^4 and 10^5 s. The photo-induced absorption has hysteresis characteristics, which can be seen at the diagram of the corresponding absorption coefficients k_{600}–k_{800} for the development of the absorption during the excitation–relaxation processes.

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